SECOND VIRIAL AND ZERO-PRESSURE JOULE-THOMSON COEFFICIENTS OF POLAR AND NONPOLAR GASES AND GAS MIXTURES

M. P. SAKSENA, V. P. S. NAIN AND S. C. SAXENA

DEPARTMENT OF PHYSICS, UNIVERSITY OF RAJASTHAN, JAIPUR, INDIA

(*Received June* 15, 1966 ; *Resubmitted September* 19, 1966).

ABSTRACT. The second virial data of a few binary mixtures involving polar gases have been interpreted on the basis of rigorous theory in conjunction with the Stockmayer potential. The two forms have been used which differ from each other in the overlap part. Conventional combination rules have been used to approximate the unlike interaction from the knowledge the of related like interactions. The interpretation is made less ambiguous by suitably categorising the mixtures. The data of second virial of some nonpolar and polar gases, and Joule-Thomson coefficient of ammonia are discussed.

INTRODUCTION

Hirschfelder, McClure and Weeks (1942), and Rowlinson (1949) employed the following Stockmayer (12-6-3) potential :

$$\phi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] - \frac{\mu^2}{r^3}\, g(\theta_1, \theta_2, \psi), \qquad \ldots \quad (1)$$

where

$$g(\theta_1, \theta_2, \psi) = 2\cos_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos\psi \qquad \ldots \quad (2)$$

to compute the second virial coefficient of polar gases. Here $\phi(r)$ is the interaction potential energy of the molecules at a separation distance r, θ_1 and θ_2 are the inclinations of the two dipole axes to the intermolecular axis, ψ is the azimuthal angle between them, μ is the permanent dipole moment, and ϵ and σ are the two potential parameters. Saxena and Joshi (1962) suggested another potential differing from that of Eq.(1) in its steepness for the overlap part of the potential. It has the explicit form similar to that of Eq.(1) except the repulsive force index is chosen to be eighteen and ϵ_0 has been preferred for ϵ. The two are simply related as,

$$\epsilon = \delta\epsilon_0/3\sqrt{3}. \qquad \ldots \quad (3)$$

The potential parameters ϵ or ϵ_0 and σ are determined by analysing the experimental data of second virial, $B(T)$, as a function of temperature, while those for mixtures can be obtained by the geometric mean rules for ϵ or ϵ_0, and arithmetic mean rule for σ. The expressions for $B(T)$ of pure gases, B_{mix} for binary mixtures and Joule-Thomson coefficient μ^0 for pure gases are given by Hirschfelder, Curtiss

and Bird (1964). The potential parameters from the literature *as well as* determined afresh by us are recorded for pure gases in Table I and for mixtures in Table II.

In this article we interpret the second virial data for pure gases and mixtures on the above two potentials. The gas systems considered involve both polar as well as nonpolar gases. A special effort has been made to present as far as possible an unambiguous interpretation and in many cases such conclusions are possible while for the remaining this will be possible only after a clearer knowledge of the association properties of the polar molecules is acquired.

$B(T)$ and $\mu^0 C_p^0$ for pure gases

The calculated and experimental values of $B(T)$ for the three nonpolar gases C_6H_6, C_6H_{12} and n-C_6H_{14}, as a function of temperature in the range where experimental data exist are shown in Fig. 1. The comparison of theory and experiment for the two polar gases chloroform and diethyl-ether is shown in Fig. 2. In Figures 1 and 2 the continuous line represents the $B(T)$ values calculated according to the (18-6) and (18-6-3) potentials respectively, while the dotted line similarly corresponds to the (12-6) and the (12-6-3) potentials respectively. A similar comparison for the three remaining polar gases has already been given earlier by Saxena and Joshi (1962a). The experimental data of μ^0 are very scarce and of all the gases discussed here experimental values are available only for ammonia. We show in Fig. 3 these experimental points compared with the theoretical values on (12-6-3) and (18-6-3) potentials. A critical look of these three figures along with similar earlier studies reveal some interesting and useful information. In what follows below we discuss such aspects.

For the three gases of Fig. 1 we find that the scatter in the experimental points is appreciable. This particularly bothers us, for all these three gases there

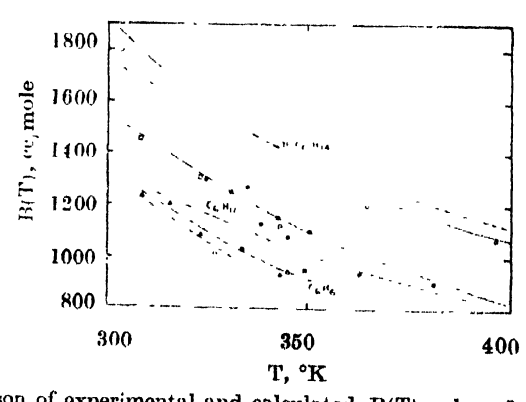

FIGURE 1. Comparison of experimental and calculated B(T) values for pure nonpolar gases as a function of temperature 0, ●, □, ■, Δ and ▲ are experimental points, continuous and dashed curves refer to (18-6-3) and (12-6-3) potentials respectively.

is also appreciable difference between the two sets of computed values. Still if one tries to compare the theoretical curves with a sort of mean experimental curve some preference follows for the (18-6) potential. Saxena and Joshi (1962b) studied seven gases (neo-C_5H_{12}, C_2N_2, C_3H_4, SiF_4, SF_6, C_2H_6 and CH_4) and found that except for neo-C_5H_{12} where (12-6) potential is inferior, both the potentials are equally well in reproducing the experimental data which are also more consistent than that of Fig. 1. Saksena and Saxena (1966) further studied the gases CO_2, N_2O, C_2H_4 and N_2 and found that the two potentials are almost equally good. This however is as expected, for in almost all cases we are sufficiently below the Boyle point and in this region only the attractive part of the potential plays a significant role and that happens to be common in form and approximately equal in magnitude for both these potentials. We should expect that for temperatures above Boyle point the two potentials will appreciably differ and here (18-6) potential is likely to give a lead.

Saxena and Joshi (1962a) studied ten polar gases (CH_3Cl, C_2H_5Cl, $(CH_3)_2CO$, CH_3OH, CH_3F, CH_3NO_2, CH_3CHO, NH_3, H_2O and CH_3CN) on the (18-6-3) potential. This work has been extended to include two more gases here viz., $CHCl_3$ and $(C_2H_5)_2O$. Fig. 2 indicates that both the potentials are almost equally good

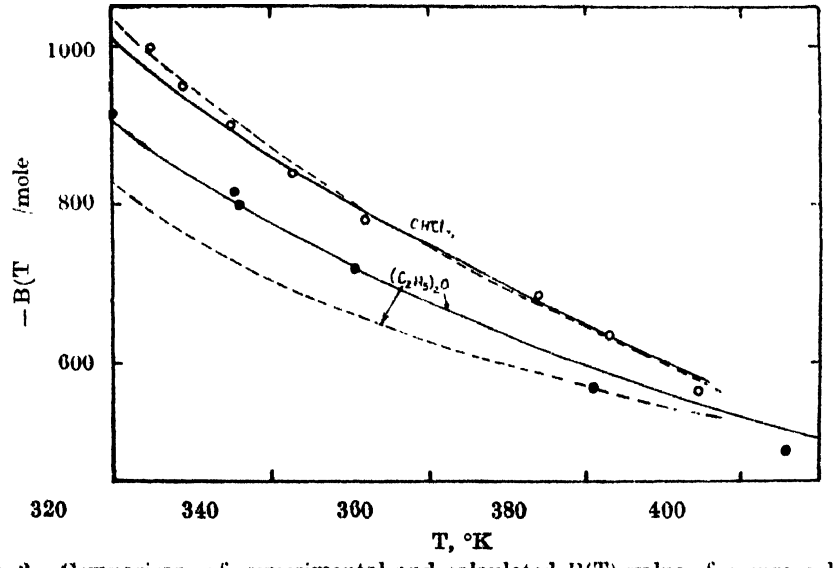

Fig. 2. Comparison of experimental and calaulated B(T) values for pure polar gases as a function of temperature 0 and ● are experimental points, continuous and dashed curves refer to (18-6-3) and (12-6-3) potentials respectively.

in reproducing the experimental data. The differences in the two sets of computed values, here as well as in the earlier work, are insignificant. This however should not be regarded as disappointing for the same reasons as mentioned above for the nonpolar gases.

In duscussing the second virial of nonpolar and polar gases above we have not taken into account the effect of association between the molecules. The

formation of dimers and assemblies involving still larger number of a molecules is more pronounced for polar than for nonpolar molecules. Lambart *et al* (1949) and Fox and Lambert (1951) have suggested that the degree of association and its influence on the second virial should be estimated from the difference of the observed values and that obtained on the basis of Berthelot's equation. Lambert *et al* (1949) have shown that the degree of association is appreciable for acetonitrile and acetone only while chloroform and diethyl ether hardly show any such tendency. These authors (1949) and Rowlinson (1949) have further shown that the potential energy curve is seriously altered in presence of association. The depth of the potential energy, the position of the minimum and the general shape all get changed. This has a serious impact with out work described here as also with the large amount of work available in the literature which are also based on a similar approach. These efforts derive incentive from the possible facts that association and its effect on $B(T)$ may be small and more in the plausibility of finding such effective values of the potential parameters which can approximate the observed facts tolerably well. This has its own practical utility. Though some work has been done to disentangle the contributions to virial by the association over the free molecule, still much remains to be done to permit any accurate assessement.

A more sensitive property for finding out the appropriateness of a potential is the zero pressure Joule-Thomson coefficient. This theoretical possibility is completely offset by the unavailability of appropriate data. The experimental data are available only for water and ammonia. Both these systems have large dipole and appreciable quadrupole moments and therefore the potential so far discussed are inappropriate. Saxena and Joshi (1962) therefore extended the rigid dipole model of equation (1) by considering the term arising from the interaction of the permanent dipole and its induced dipole. This point polarizable model was considered by them to explain the second virial coefficient of a

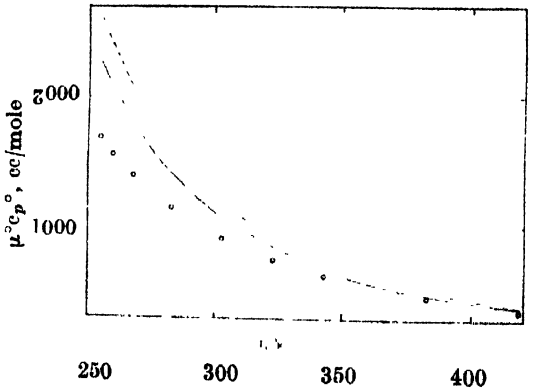

Fig. 3. Comparison of experimental and theoretical $\mu^\circ C_p^\circ$ values for ammonia as a function of temperature. 0 are experimental points, continuous and dashed curves refer to (18-6-3) and (12-6-3) potentials respectively.

few gases. They found a real change in the values of the potential parameters. Saxena, Joshi and Ramaswamy (1963) found it impossible to correlate $B(T)$ and $\mu^0 c^\circ_p$ data for water on the basis of a single (12-6-3) or (18-6-3) potential. The reason is obvious. Here also we find from Fig. 3 that $\mu^0 c^\circ_p$ exerimental values for ammonia are not well reproduced by theory. It may be noted that (18-6-3) potential leads to better agreement with the experiment than the (12-6-3) potential. This may not be regarded as enough proof for the superiority of the (18-6-3) over the (12-6-3) but due regard may be given of the likely better conpetence of (18-6-3) potential for correlation. This point which looks rather trivial is important when one recalls that the computation of $B(T)$ on a potential appropriate for this gas will not be an easy job even for present age fast speed computers

$B(T)$ for gas Mixtures

The second virial coefficient for binary gas mixtures involving polar gases have not been studied so far on the basis of the rigorous kinetic theory. There are many reasons for this indifference. The important ones are the scarcity of experimental data and lack of theoretical elegance to account for the association effects in polar molecules which now appear in a more complicated fashion than for pure gases. We endeavour to cut through this inertia and see how best this comparison of theory and experiment can be made. We find that experimental data are available on six binary gas pairs permuting out of the polar and nonpolar gases discussed in the last section. The systems are *n*-hexane-diethyl ether, *n*-hexane-chloroform, chloroform-diethyl ether, cyclohexane-acetonitrile, cyclohexane-acetone and benzene-chloroform. The data on the first two systems are of Fox and Lambert (1951), fr the next three systems of Lambert, Murphy and Sanday (1954), and for the last pair of Francies and McGlashan (1955) as reported by Huff and Read (1963). We next propose to investigate these data in following arbitrarily chosen categories :

1. In this we will consider those mixtures which include a combination of nonpolar gas with such a polar gas which does not exhibit any tendency to associate.

2. Those pairs which comprise a nonpolar and such a polar gas which dimerizes only.

3. And here such gas pairs in which both the components are polar but the gases are such which do not exhibit the tendency of association individually i.e. in the pure state but do so when two different gases interact.

4. There are other categories also possible. For example when two polar gases form a mixture these individually dimerize but may or may not do so in the mixture form. The six gas pairs mentioned above fall in the first three categories *n*-hexane-diethyl ether, *n*-hexane-chloroform and benzene-chloroform belong to

the first category, cyclohexane-acetonitrile and cyclohexane-acetone to the second category while diethyl ether-chloroform to the third category. There are some measurements available also on such gas pairs which fall in the categories mentioned in 4 above. We defer any consideration of such systems for the time being because a lot of ambiguity gets involved due to the polymerisation of like and unlike molecules. As soon as our understanding is improved about the association properties of molecules it will be profitable to study such systems and derive some inferences from this somewhat resolved and unambiguous study.

In Table III are reported the experimental and theoretically calculated values of the quantity B_{12} on both the potentials. It is known that in such studies B_{12} is preferred than B_{mix} because the former is independent of composition and is sensitively controlled by the nature of unlike interaction. Of all the possible combinations such mixtures which fall in the first category are easiest to interpret and the calculations approximate the ideal requirements as far as possible. In general, the agreement between both the sets of calculated and experimental values may be regarded as satisfactory. However, there are some interesting details which deserve special mention, here again the limitation of the data as regards the temperature range comes as a serious handicap. The agreement between theory and experiment for pure gases is usually better than for B_{12} obtained in these cases. The improvement here also can be easily obtained in case the unlike parameters are determined from B_{12} instead of the combination rules as is done for the case of pure gases. The principle reason for not following this approach and instead employ the combination rules is however obvious and as mentioned earlier lies in the limited information of the mixture virials. It would be a great valuable contribution to produce such data over an extensive temperature range so that unlike interaction may be directly determined and thence the adequacies of combination rules. This approach will have a sound backing and will have the competence to throw some real genuine light on the suitability of an intermolecular potential. For the first two systems of Table 3 we find that (12-6-3) potential is somewhat preferable than (18-6-3) potential. This is somewhat of an illusion when one recalls that for the common constituent of these two mixtures, *n*-hexane, (18-6-3) potential was distinctly superior over the (12-6-3) potential as was also for diethyl ether though for coloroform the difference is not very pronounced. These comments then suggest that the fault lies probably with the combination rules for the (18-6-3) potential. But as the rules for these two potentials are likely to be identical in nature the alteration in one to improve the agreement with experiment will spoil in the other. We strongly feel that it is not advisable to make an attempt to alter these combination rules which have withstood many crucial tests but to feel satisfied with the general overall success achieved. This suggestion which may be regarded as provisional at the moment should be throughly investigated as soon as the experimental data have become

available. For the third system of Table III where five directly observed points are available we find that (18-6-3) potential leads to a better agreement with the experiment than the (12-6-3) potential. Thus, in view of the present work for the three binary systems and the related pure gases we find that (18-6-3) potential seems a bit more promising for correlation than the (12-6-3) potential.

Fox and Lambert (1951) have studied the first two systems of Table III using Berthelot equation for the second virial coefficient derived on the basis of the principle of corresponding states. They concluded that these systems do not exhibit any tendency for association. A similar remark holds for the pure components involved. Thus the theory of virials applied adequately for such nonpolar-polar combinations and theoretical calculations may be given as much reliance as mixtures of nonpolar gases.

TABLE 1

Like interaction parameters for the (18-6-3) and (12-6-3) potentials*

Gas		μ Debye	l^*	ε/k or ε_0/k °K	σ Å	b cc/mole	Reference
n-hexane	(a)	—	—	639	4.07	85.05	Present work
	(b)	—	—	643.5	5.01	158.11	
Cyclohexane	(a)	—	—	562	4.40	107.5	Present work
	(b)	—	—	680	4.60	122.82	
Benzene	(a)	—	—	567	4.26	97.44	Present work
	(b)	—	—	974	3.50	54.1	
Chloroform	(a)	1.05	0.10	633	3.57	57.62	Present work
	(b)		0.10	1060	2.98	33.45	H.C.B. (1964)
Diethyl ether	(a)	1.1	0.11	595	3.62	59.73	Present work
	(b)		0.10	888	3.36	43.08	
Acetone	(a)	2.74	0.88	389	3.83	70.85	Sexena & Joshi (1962a)
	(b)		0.7	520	3.76	66.87	H.C.B. (1964)
Acetonitrile	(a)	3.5	1.60	349	4.10	86.94	Saxena & Joshi (1962a)
	(b)		1.2	400	4.02	82.04	H.C.B. (1964)
Ammonia	(a)	1.47	1.10	257	2.70	24.83	Saxena & Joshi (1962a)
	(b)		1.0	320	2.60	22.12	H.C.B. (1964)

*(a) indicates the potential parameters for the (18-6-3) while (b) for the (12-6-3). $b=(2/3)\pi N\sigma^3$, N being Avagadro number.

TABLE II

Unlike interaction parameters for the (18-6-3) and (12-6-3) potentials.*

Gas system		t^*	$(\varepsilon_0)_{12}/k$ or ε_{12}/k °K	σ_{12} Å	b_{12} cc/mole
n-hexane-Chloroform	(a)	—	634	3.82	70.3
	(b)	—	826	3.99	80.2
n-hexane-Diethyl ether	(a)	—	617	3.85	56.8
	(b)	—	756	4.18	92.2
Cyclohexane-Acetone	(a)	—	468	4.12	87.9
	(b)	—	595	4.18	92.2
Cyclohexane-Acetonitrile	(a)	—	443	4.25	96.8
	(b)	—	522	4.31	101
Chloroform-Diethyl ether	(a)	0.105	614	3.60	58.6
	(b)	0.10	970	3.17	40.2
Benzene-Chloroform	(a)	—	599	3.91	75.4
	(b)	—	1016	3.24	42.9

*(a) indicates the potential parameters for the (18-6-3) while (b) for the (12-6-3). $b_{12} = (2/3)\ \pi N \sigma_{12}^3$.

TABLE III

Comparison of the calculated and experimental $-B_{12}$ (cc/mole) values

Gas System	T °K	Experimental	Calculated	
			(18-6-3)	(12-6-3)
n-Hexane-Diethyl ether	326.2	1130	1067	1090
	352	940	879	928
n-hexane-Chloroform	326.2	1190	1131	1134
	352	960	937	970
Benzene-Chloroform	315.7	1300	1131	1103
	323.2	1130	1071	1039
	333.7	1040	988	957
	343.2	960	928	884
	349.3	950	890	843

TABLE IV

Comparison of the calculated and experimental $-B_{mix}$ (cc/mole) values

Gas system	T °K	Mole-fraction of non-polar component	Experimental	Calculated (18-6-3)	Calculated (12-6-3)
Cyclohexane-Acetonitrile	326	0.2	2445	2530	2637
		0.5	1500	1558	1549
		0.8	1250	1210	1158
	349	0.2	1795	1819	1870
		0.5	1130	1172	1173
		0.8	960	935	892
Cyclohexane-Acetone	326	0.2	1267	1266	1241
		0.5	1146	1054	1040
		0.8	1169	1077	1100
	349	0.2	1023	1036	1027
		0.5	961	898	875
		0.8	1026	960	926

TABLE V

Comparison of the calculated and experimental $-B_{12}$(cc/mole) values for Chloroform-Diethyl ether mixtures

T °K	Experimental	Calculated (18-6-3)	Calculated (Corresponding states)	Calculated (12-6-3)
326.2	1520	906	860	840
338	1290	827	800	764
352	1030	750	730	693
363	870	697	680	643
393	500	581	550	539

The two systems elaborated in Table IV form the second category and here the two polar gases involved viz., acetonitrile and acetone polymerise but such effects are absent between the cyclohexane-acetonitrile and cyclohexane-acetone molecules in combination. This assumption which conforms the actual state for both these pairs offers a simplified procedure for an unambiguous interpretation of the experimental results. The pure polar gases no doubt have large association as pointed out by Lambert *et al*(1949). but in the calculation of B_{mix} this is easily taken care of by putting the observed value for the pure virial. As there is no association between the uhlike molecules B_{12} remains unaffected. Computed values of B_{mix} for both the potentials are recorded in Table IV as function of composition at a particular temperature. We have for these systems considered B_{mix} values instead of B_{12} because it was found that it is not possible to uniquely

choose a single value of B_{12} for the entire of composition. This is an important observation and may have its bearing on the fact that one component of the mixture polymerises individually and consequently this is a property of all systems which belong to this category. It is pleasant to note in the Table that in all cases theory and experiment are in good agreement. This we regard as particularly important and a good support for the assumptions made to explain the behaviour of systems falling in this group. The two potentials in almost all cases lead to fairly identical results though if we critically examine (18-6-3) potential is a bit superior.

The data for one system, chloroform-diethyl ether, where both the components are polar, conform to the category third. They however show association when in combination. The estimation of B_{12} therefore from theory will not be directly comparable to the observed values because in theory we have not taken into account such effects. In fact the computed values should fall short to the directly observed values. In Table V we have listed the experimental B_{12} values as a function of temperature along with the computed values on the two potentials for the system. Indeed it will be noticed that the experimental values are always much higher than the calculated values and are in complete conformity with the prediction of the Berthelot's equation.

CONCLUSIONS

This study reveals several very interesting indications and inferences. The limitations of the availability of the appropriate type of data came in the way to extend the comparison of theory and experiment on a more elaborate level. This naturally puts an hesitation in emphasizing the particular features this paper has brought into light but still it is worthwhile as well as advisable to sum up what may be called as provisional conclusions to which future investigations should purport to strengthen. These are,

1. Properties of mixtures involving polar gases are not amenable to that straightforward interpretation as in the case of nonpolar gases. Some caution and care however in many cases may enable a thorough dependable interpretation. The knowledge of dipole and higher order moments, and the association properties of the molecules are big help for such a study.

2. The two potentials (12.6-3) and (18-6-3) used for the first time to interpret the mixture data are found as successful as the corresponding potentials for nonpolar gases in all those cases where their applicability is permissible.

3. Partly enlightened by our experience of (18-6) and (12-6) potentials for nonpolar gases and gas mixtures, we find the symptoms suggesting that the steeper (18-6-3) potential may prove better for correlation of polar gas behaviour also at high temperatures and we look forward to put this prediction to an actual

test as soon as the proper data become available. This belief stems out from several indications where (18-6-3) is found superior to (12-6-3).

4. The categorisation of mixtures involving polar gases suggested here is arbitrary and artificial but has its basis in great convenience of interpretation and similarity of behaviour. It makes possible to think that combinations of polar and nonpolar gases which do not associate individually or in combination are easily interpretable like mixtures of nonpolar gases. Such combinations in which polar component associates while its other nonpolar partner as well as the combination do not, we find correlation of B_{mix} is possible. This approach is not quite free from objection for the representation of the polar gas behaviour by such an approach is an approximation. How to modify the theory to user the association effects is still a problem to solve adequately. However the present effort suggests a bold easy wayout for the time being. We also find that the contribution to virial is very large when the combination of two pure components only exhibits association. Obviously the situation will become still more delicate when pure molecules will also show such association individually.

5. In interpreting the results we find that it is of great importance to know how far association effects are possible in individual molecules and when they combine. Unfortunately at the moment no definite procedure exists to do such a calculation though some efforts in this direction are being made recently. The use of Berthelot's equation to estimate qualitatively the presence of association is also only a rough approximation.

ACKNOWLEDGMENTS

We are thankful to the Ministry of Defence and the Council of Scientific and Industrial Research, New Delhi, for supporting this work. The awards of senior and junior research fellowships to M.P.S and V.P.S. respectively are also gratefully acknowledged.

REFERENCES

Buckingham, A. D. and Pople, J. A., 1955 *Trans. Farad. Soc.*, **51**, 1173.
Fox, J. H. P. and Lambert, J. D., 1957, *Proc. Roy. Soc. (London)* **A201**, 557.
Francis, P. G. and McGlashan, M. L., 1955, *Trans. Farad. Soc.* **51**, 593.
Hirschfelder, J. O., McClure, F. T. and Weeks, I. F., 1942, *J. Chem. Phys.* **10**, 201.
Hirschfelder, J. O., Curtiss, C. F. and Bird, R. B., 1964, *Molecular Theory of Gases and Liquids*, John Wiley & Sons, Inc., New York.
Huff, J. A. and Reed, T. M., 1963, *J. Chem. Eng. Data* **8**, 306.
Lambert, J. D., Murphy, J. J. and Sanday, A. P., 1954, *Proc. Roy. Soc. (London)* **A226**, 1954.
Lambert, J. D., Roberts, G. A. H., Rowlinson, J. S. and Wilkinson, V. J., 1949, *Proc. Roy. Soc. (London)* **A196**, 113.
Rowlinson, J. S., 1949, *Trans. Farad. Soc.* **45**, 974.
Saksena, M. P. and Saxena, S. C., 1966 *Proc. Natl. Inst. Sci. (India)*, **32**, 170.
Saxena, S. C. and Joshi, K. M., 1962a, *Phys. Fluids*, **5**, 1217.
——————————— 1962b, *Indian J. Phys.*, **36**, 422.
Saxena, S. C., Joshi, K. M. and Ramaswamy, S., 1963, *Indian J. Pure and Appl. Phys.* **1**, 420.